

Designer Patterns: Flexible Control of Precipitation through Electric Currents

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(Dated: February 19, 2008)

Precipitation patterns generated by $A^+ + B^- \rightarrow C$ type reaction-diffusion processes are studied. It is shown both theoretically and experimentally that the patterns can be controlled by an appropriately designed, time-dependent electric current in the system. We describe examples of current dynamics yielding periodic bands of prescribed wavelength, as well as more complicated structures. The pattern control is demonstrated experimentally on the reaction-diffusion-precipitation process $2\text{AgNO}_3 + \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{Ag}_2\text{Cr}_2\text{O}_7 + 2\text{KNO}_3$ taking place in a gel.

PACS numbers: 64.60.My, 82.20.-w, 89.75.Kd

Spontaneous pattern formation can be observed at all lengthscales [1] and much effort has been devoted to gaining insight into the dynamics of these processes [2]. One of the aims of these studies is to reproduce and control the emerging patterns, thereby opening possibilities for technological applications such as downsizing electronic devices [3]. We focus here on an important class of reaction-diffusion systems yielding precipitation patterns [4]. Since these patterns emerge in the bulk, they have been studied recently in connection with the so-called *bottom-up* (bulk) design methods, as contrasted to *top-down* ones where material is removed to create structures (as e.g. in case of lithography). It has been found that the precipitation patterns can be influenced by appropriately chosen geometry [5], boundary conditions [6], or by a combined tuning of the initial and boundary conditions [7, 8]. The above control methods are straightforward but unwieldy, and more flexible approaches are clearly needed. Here we introduce a novel method based on the use of pre-designed electric currents for regulating the dynamics of the reaction zones in the system. The power of this method is verified experimentally by producing periodic precipitation patterns with controlled spacing, as well as more complex structures.

Our idea stems from the observation that precipitation patterns are often formed in the wake of moving reaction fronts [2, 4]. The motion and reaction dynamics of the front determine where and when the concentration of the reaction products crosses threshold levels thus inducing precipitation. Consequently, and this is the essence of our proposal, control over the precipitation pattern can be realized through *controlling the properties of the reaction front*. In order to explain how this can be done, we turn to the concrete example of Liesegang patterns [4, 9].

In a somewhat generic description, the Liesegang dynamics consists of the reaction $A^+ + B^- \rightarrow C$ of the ions of two electrolytes $A \equiv (A^+, A^-)$ and $B \equiv (B^-, B^+)$, followed by the precipitation of the reaction product C . The electrolytes are initially separated (see Fig. 1 for a

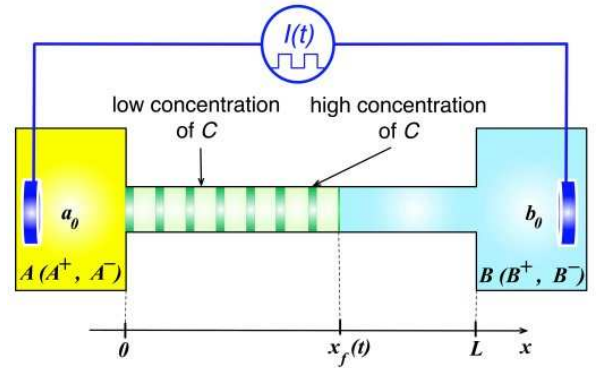


FIG. 1: Experimental setup for producing Liesegang precipitation patterns as described in the text. The controlling agent is the generator providing electric current $I(t)$ with a prescribed time-dependence.

typical experimental setup) with the inner electrolyte B homogeneously dissolved in the gel inside a tube. The outer electrolyte A is in an aqueous solution which is brought into contact with the gel at the start of the experiment. The initial concentration a_0 of A is much larger than that b_0 of B and, consequently, A invades the gel and a *reaction front* forms and moves along the tube.

The relevant properties of this front in the absence of an electric field are simple and well-known [10, 11]:

- (i) The width of the front is practically negligible.
- (ii) The front moves diffusively, i.e., its position along the tube is given by $x_f(t) = \sqrt{2D_f t}$, with the diffusion coefficient D_f determined by a_0 , b_0 , and the diffusion coefficients of the reagents.
- (iii) The concentration c of the reaction product C left in the wake of the front is constant, $c = c_0$. The value of c_0 depends on a_0 , b_0 , the diffusion coefficients, and on the rate k of the reaction $A^+ + B^- \xrightarrow{k} C$.

The second step in the pattern formation, namely the phase separation of the C -s, takes place only if their local concentration c is above a precipitation threshold, $c > c^*$.

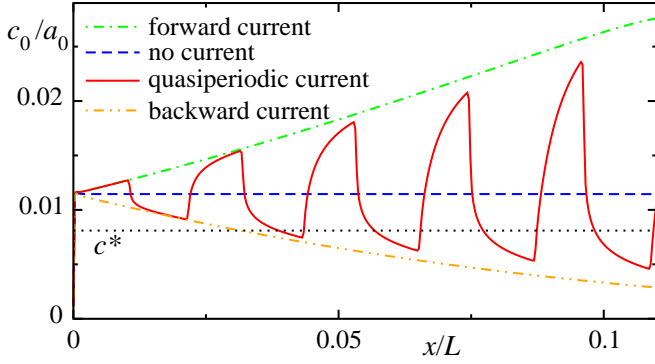


FIG. 2: Concentrations of the reaction product in the wake of the front, in the absence of a current, respectively when a constant forward or backward current, or a quasiperiodic current (changed at times $\tau n^2/2$) is switched on.

The experimental setup is thus chosen so that $c_0 > c^*$. The precipitation pattern itself is then the result of a complex interplay of the production of C -s by the front and the ensuing phase separation dynamics in the wake of the front. Namely, the front produces a precipitation band at the beginning since $c_0 > c^*$ just behind the front. This band acts as a sink for the newly produced C -s and thus their concentration in the front decreases below c^* . As the front moves far from the existing band, the depletion effect diminishes and the c in the front can again exceed c^* thus leading to the formation of the next band. A quasiperiodic reiteration of the above process yields the Liesegang patterns (lowest panel in Fig.4). The positions x_n ($n = 0, 1, \dots$) of the bands obey the spacing-law, i.e., they form a geometric series $x_n \sim (1 + p)^n$ ($p > 0$), as observed in experiments and reproduced by various theories [11, 12].

Since the precipitation is always initiated in the front, the position of the band x_n and its time of formation t_n are related by the so-called *time-law*,

$$x_n = \sqrt{2D_f t_n}. \quad (1)$$

From this equation one concludes that the positions x_n of the precipitation bands can be regulated either by modifying the time-law, or by controlling the t_n -s.

The first attempts to change the functional form of the time-law were based on the idea that the reaction takes place between ions $A^+ + B^- \rightarrow C$, therefore the motion of the front is potentially affected by applying a *constant external electric field* [13, 14, 15, 16, 17, 18]. The results of both the experimental and theoretical investigations suggest, however, that neither the locality (i), nor the diffusive nature (ii) of the front are altered significantly by a constant electric field, i.e., the time-law (1) is practically not modified for the parameter range of interest in the experiments. The constant electric field has, however, an important effect on property (iii) of the front. It was found [17] that for a *forward field* (i.e., a field that

drives the ionic reagents towards each other), the concentration c increases linearly in the direction of the front motion. A *backward field* yields a decreasing concentration of C -s; this decrease is linear at the beginning and leads finally to the complete extinction of the reaction.

The above results equally apply to the case where a *current generator* is used (Fig. 1) to produce constant backward and forward currents, as illustrated in Fig. 2. The new results in Fig. 2 (continuous curve) concern the case when the applied current is constant in absolute value, but changes sign quasiperiodically at times $\tau n^2/2$, with τ giving a timescale and $n = 0, 1, 2, \dots$.

Figure 2 together with the time-law (1) provide us the key to create precipitation bands at *arbitrarily predefined locations*, by using an appropriately-designed time-dependent current $I(t)$. Indeed, given a set of prescribed band positions x_n , one switches on the forward current at times $t_n = x_n^2/2D_f$. This increases the concentration of C -s to cross the precipitation threshold and thus a band forms at x_n . In order to avoid spontaneous formation of spurious bands one must switch on a backward current at some intermediate times between t_n and t_{n+1} .

The above protocol works, in particular, for producing the much sought after *periodic Liesegang pattern*. One can obtain a controlled wavelength d such that $x_n = dn$ by switching on the forward current at $t_n = (2n)^2\tau/2$, where $\tau = d^2/2D_f$. If the desired period d is smaller than half the *local wavelength* of the Liesegang pattern, then the spurious bands can be avoided by switching on the backward current when the front is halfway between x_n and x_{n+1} , i.e., at times $(2n+1)^2\tau/2$.

In order to put the above argument on a more solid foundation, we extended our previous model of Liesegang pattern formation in the presence of an electric field [17, 18] to the case of a time-dependent current flowing through the system. The first stage of the process is described by the evolution equations for the concentration profiles of the ions $a^\pm(x, t)$ and $b^\pm(x, t)$, with the underlying electroneutrality hypothesis. These equations take a relatively simple form for the case of monovalent ions with equal diffusion coefficients,

$$\partial_t a^+ = D\partial_x^2 a^+ - j(t)\partial_x(a^+/\Sigma) - ka^+b^- \quad (2)$$

$$\partial_t b^- = D\partial_x^2 b^- + j(t)\partial_x(b^-/\Sigma) - ka^+b^- \quad (3)$$

$$\partial_t a^- = D\partial_x^2 a^- + j(t)\partial_x(a^-/\Sigma) \quad (4)$$

$$\partial_t b^+ = D\partial_x^2 b^+ - j(t)\partial_x(b^+/\Sigma). \quad (5)$$

Here $j(t) = I(t)/\mathcal{A}$ is the externally controlled electric current-density flowing through the tube of cross section \mathcal{A} , $\Sigma = q(a^+ + a^- + b^+ + b^-)$ with q being the unit of charge, and D is the diffusion coefficient of the ions. The reaction rate k is usually large resulting in a reaction zone of negligible width.

The second stage in the process, namely the phase separation of the reaction product C , is modeled by the Cahn-Hilliard equation with a source term describing the

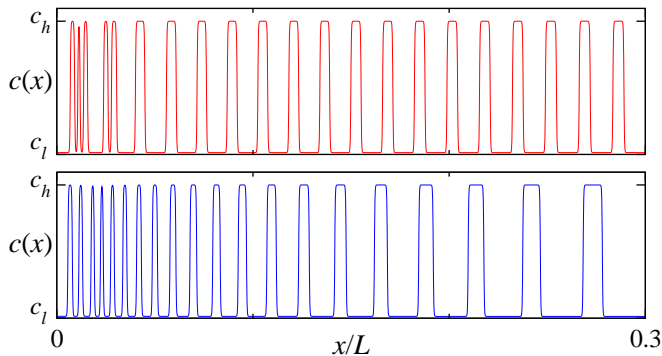


FIG. 3: Theoretical precipitation patterns. The periodic pattern emerging in the presence of a quasiperiodic current (upper panel) as compared to the usual Liesegang band-structure obtained in the absence of current (lower panel). The values c_h and c_l are the stable concentrations of C .

rate of production of C -s in the reaction zone [12, 18]. The free energy underlying the thermodynamics is assumed to have a Ginzburg-Landau form with minima at some low (c_l) and high (c_h) concentrations of C . Using then a shifted and rescaled concentration $m = (2c - c_h - c_l)/(c_h - c_l)$, yields the following equation

$$\partial_t m = -\lambda \Delta(m - m^3 + \sigma \Delta m) + S(x, t) \quad (6)$$

where $S(x, t) = 2ka^+b^-/(c_h - c_l)$ is the source term coming from the equations (2-5) of the first stage. The parameters λ and σ can be chosen so as to reproduce the correct time and lengthscales in experiments [18, 19].

Equations (2-6) constitute the mathematical formulation of the problem. They can be solved e.g. by the classical fourth-order Runge-Kutta method. Examples of emerging patterns in case of quasiperiodic current (periodic pattern) or without current (standard Liesegang pattern) are shown in Fig. 3 [21]. We tested our theory on a much-studied case where a precipitate of silver dichromate ($\text{Ag}_2\text{Cr}_2\text{O}_7$) is formed due to the reaction of silver nitrate (AgNO_3) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in a gelatine gel. In this system, various structures have been observed (regular patterns, spirals, helixes [20]), and the effect of a constant electric field [15] has also been studied. The experiments were carried out in vertical glass tubes (diameter: 1 cm, length: 20 cm) containing a gelatine gel column (length: 13 cm) closed by agarose gel stoppers (length: 1.5 cm). The inner electrolyte was dissolved in the gel [3.0 g gelatine (Reanal) added to 50 cm³ of 0.0036 mol/dm³ $\text{K}_2\text{Cr}_2\text{O}_7$ (Reanal) solution] while the outer electrolyte [2 cm³ of AgNO_3 solution (Reanal, 2.50 mol/dm³)] was placed on top of the gel at the start ($t = 0$) of the experiments. Ni electrodes were fixed at the top and the bottom of the gel and the current was supplied by a programmable current generator (Keithley 2410 Source Meter). Initially, the current generator maintained a forward current (the upper electrode in the AgNO_3 solution was positive). The

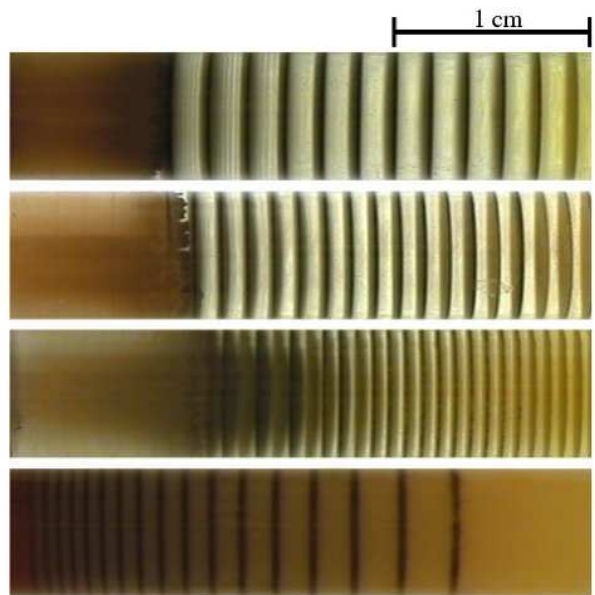


FIG. 4: Experimental precipitation patterns. A quasiperiodic current of amplitude 500 μA was used with $\tau = 4, 2$, and 1 min, respectively, as going down the panels. Lowest panel illustrates the usual Liesegang bands.

current was then changed from forward to backward and vice versa every $\tau n^2/2$ seconds. At $t = 0$, the outer electrolyte started to diffuse into the gel and, as the reaction front advanced along the tube, a brown $\text{Ag}_2\text{Cr}_2\text{O}_7$ precipitate emerged in the form of bands. The experiments were run usually for two days, followed by taking pictures of the resulting pattern in transmitted light.

Different types of experiments were performed. First, in the absence of electric current, usual Liesegang bands were produced (lowest panel of Fig 4). Second, a quasiperiodic electric current of a few hundred μA amplitude is switched backward and forward at times $\tau n^2/2$. The resulting periodic patterns for various τ -s are shown in the three upper panels of Fig. 4. As can be seen on Fig. 5, the wavelengths d of the patterns show the $\sqrt{\tau}$ -dependence in agreement with the theoretical predictions. It is also remarkable that the wavelengths are not affected by the intensity of the electric current used in the experiments (250, 500, and 1000 μA). We note that, occasionally, secondary patterns appear with a wavelength an order of magnitude smaller than d (see the first three band-gaps in the upper panel of Fig. 4). It is not quite clear under which experimental conditions these secondary patterns form, though they can be observed more frequently when d is larger. Our theory does not account for such features.

A third series of experiments was devoted to demonstrate the feasibility of creating more complex patterns. Figure 6 shows an example where equidistant bands are followed by a predesigned structure consisting of groups of 2, 3, and 2 bands separated by voids. This "2-3-2"

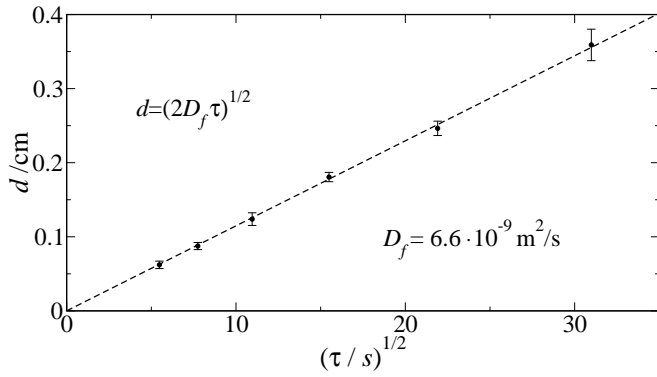


FIG. 5: Characteristic wavelength d of the pattern generated by switching the current forward and backward at times $\tau n^2/2$. The front diffusion coefficient D_f is the result of a linear fit.

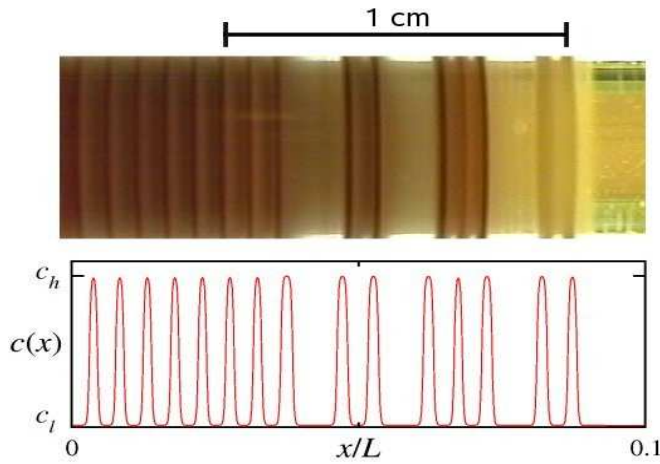


FIG. 6: An example of designer pattern. The proposed protocol for generating the "2-3-2" structure is verified both in the experiment (upper panel) and in the theory (lower panel), as described in the text.

pattern was generated by taking the protocol for a periodic pattern, and making two modifications. Namely, voids are generated by substituting the forward with a backward current and, furthermore, the amplitude of the backward current was always half of the forward one. Here again, the experimental results are in excellent agreement with the theoretical predictions (Fig. 6). Our results on the control of precipitation patterns have several important implications. From a theoretical point of view, they demonstrate the predictive power and, implicitly, the correctness of our *phase-separation in the presence of a moving source* basic scenario for Liesegang pattern formation [12]. Indeed, these are the first experiments which test intricate details of the theory and the agreement is excellent.

From an experimental point of view, the electric-current control of the patterns is a flexible and rather general tool, which should be useful whenever the pat-

terns emerge as the result of reactions between charged particles (ions, nano- or colloid particles). Combining this tool with more traditional ones (choice of geometry, initial concentrations, boundary conditions) opens up further possibilities for control and structure design.

One of the main motivation for finding control mechanisms is to design structures on small scales. This brings up the question about the lower limit of d obtainable by our method. Although Fig.5 does not show the existence of such a limit as τ is decreased, we should note that there are at least two effects which are not well-controlled and may limit the smallest wavelength that can be reached. They are the width of the reaction zone and the thermal fluctuations in the system. Their relevance in the down-sizing challenge remains to be understood and evaluated.

This work has been supported by the Swiss National Science Foundation and by the Hungarian Academy of Sciences (Grants No. OTKA K68109 and K68253). IL also acknowledges support from the Hungarian Academy of Sciences through the Bolyai Research Fellowship.

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